

CONCERNING THE CALCULATION OF COAL
STRUCTURAL PARAMETERS FROM SPECTROSCOPIC DATA

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Because of the heterogeneous, multicomponent nature of coal, much structural analysis work has been channelled towards the determination of parameters that can be used to describe "average" structures. In principle, FT-ir measurements can be used to quantitatively determine the aliphatic CH, aromatic CH and OH content of coal (1-5), while solid state ^{13}C nmr spectroscopy can be used to determine the relative proportions of aromatic to aliphatic carbon (6-9). There is much active research aimed at extending the scope of these techniques to allow the measurement of additional functionalities. Nevertheless, with these measurements alone a number of fundamental structural parameters (H/C , $\text{H}_{\text{al}}/\text{C}_{\text{al}}$, $\text{H}_{\text{ar}}/\text{C}_{\text{ar}}$, etc.) can be calculated. Furthermore, with the measurement of one additional parameter, the number of methyl groups (as measured by the fraction of aliphatic carbon or hydrogen involved in such groups), it should be possible to determine the distribution of aliphatic carbon (ie. the relative proportions of CH , CH_2 , and CH_3 groups) and then describe a "mean structural unit" in terms of average aromatic ring size and the type and distribution of bridging units and substituents. This can be accomplished by using the equations originally described by van Krevelen and Schuyver (10) and utilized by Dryden (11,12) for statistical structural analysis. Similar equations were also derived by Brown and Ladner (13) in order to utilize the data that was then becoming available from proton n.m.r. measurements. However, there were a number of uncertainties in applying these equations. Dryden used data from elemental analysis together with estimates of aromaticity and other parameters (eg. alicyclic hydrogen) that were to some degree uncertain. An iterative procedure was used to solve the equations. The application of the Brown-Ladner equation required assumptions concerning the aliphatic hydrogen-to-carbon atomic ratio. Quantities such as this can now be determined directly from combined FT-ir/ ^{13}C nmr measurements. We therefore considered that it might be a relatively straightforward task to calculate mean structural units for the coal samples for which we have accumulated spectroscopic data (4,9). And it is. Unfortunately, a major problem arises once we consider whether or not the numbers so derived mean anything. We will show that for an individual coal they do not. The form of the equations are such that errors accumulate dramatically and our spectroscopic measurements are insufficiently precise to obtain anything but a broad description of trends as a function of rank. We will first consider the data obtained for a set of vitrinite concentrates and specifically the problems with the FT-ir data. We will then demonstrate how even small errors in this data dramatically affect the calculation of structural parameters.

The fraction aromaticity, f_{ar} , can now be determined with what is considered to be reasonable precision by ^{13}C nmr using cross-polarization and magic angle spinning. It is probably more accurate to say that most fuel scientists are comfortable with the values of f_{ar} so derived, because there are a number of sources

of possible error and these are not easily quantified. For the sake of the arguments we wish to make here we will assume (optimistically) that the values of f_a are good to $\pm 5\%$. Values of f_a for a set of vitrinites reported previously (9) are combined with more recent measurements of additional samples by Martzel and Koenig (14) and Pugmire and Grant (15) in figure 1. There is some scatter, but a reasonably narrow band of values is apparent.

Unlike nmr measurements, where the ratio of peak areas is equal to the ratio of aromatic to aliphatic carbon, bands in the infrared spectrum require calibration. They are related to the concentration of the appropriate functional group through an absorption coefficient which is different for each band. This has led to all sorts of trouble and a variety of values of aromatic to aliphatic hydrogen ratio's can be found scattered throughout the literature. We will not discuss the various methods that can (and have) been used to calibrate infrared bands, this ground is covered elsewhere (5). In terms of the points we wish to make here, the actual values of H_{al} and H_{ar} are to some degree irrelevant, as we will be more concerned with the effects of errors in these values on subsequent calculations of structural parameters. Nevertheless, it is important and illuminating to consider one factor that is probably central to many of the discrepancies found in the literature. If we take a bituminous coal of, say 82% carbon content, we typically determine an aliphatic hydrogen content close to 4% and an aromatic hydrogen content of about 1%. There are numerous errors that can affect these measurements, but these are not simply cumulative. For example, if errors in sample preparation, band areas etc. were of the order of $\pm 10\%$, we might be able to quote values of 4-0.4% and 1-0.1% for aliphatic and aromatic CH content, respectively. However, the absorption coefficients for aliphatic and aromatic CH bands are presently being determined by equating band areas to hydrogen content determined from elemental analysis (1,5). If a sample has negligible COOH content we can write

$$H = H_{OH} + H_{ar} + H_{al} \quad (1)$$

where H is the hydrogen content determined by elemental analysis, and H_{OH} , H_{ar} and H_{al} is the hydrogen found as OH, aromatic CH and aliphatic CH, respectively. This can be rewritten as;

$$(H - H_{OH}) = I_{ar} \epsilon_{ar} + I_{al} \epsilon_{al} \quad (2)$$

where I is the intensity of the appropriate infrared band and ϵ is a conversion factor (equivalent to the reciprocal of the absorption coefficient in appropriate units) relating band area to corresponding hydrogen content. Theoretically, data from a set of coals can be used and ϵ_{ar} and ϵ_{al} determined graphically (1) or by obtaining numerical solutions to the resulting simultaneous equations (3,5). We have recently shown, however, that these equations are classically ill-conditioned (5). In other words, a range of solutions gives almost equally acceptable answers. We have spent a lot of time trying to pin down the "correct" answer, and the values we have recently come up with (5) are somewhat different to those originally reported (3). The key point here, however, is that the ill-conditioned nature of the equations means that the values of H_{ar} and H_{al} determined in this fashion are somewhat dependant. In other words, a 10% error in determining ϵ_{al} and hence H_{al} translates into a much larger error in H_{ar} . This is because the values of ϵ_{al} obtained from solutions to equation 2 will be adjusted to account for as much of the hydrogen as possible. Accordingly, if H_{al} is calculated to be 4-0.4%, H_{ar} will be calculated to be 1-0.4%. A 10% error in ϵ_{al} (hence A_{al}) translates into a 40% error in ϵ_{ar} (and H_{ar}). As a result, even

though the values of the absorption coefficients we have recently determined for the aliphatic CH stretching modes (5) are not far off the more recent values reported by Solomon (2), we still calculate vastly different values of H_{ar}/H_{al} .

Undaunted by these difficulties, we have reproduced our values of H_{ar}/H_{al} for a wide range of coals and vitrinite concentrates in figure 2. The knowledgeable reader will immediately recognize that for coals with a carbon content of 85% or higher these results are very similar to those reported by Brown (16) more than twenty five years ago. For lower rank coals Brown's results fall near the bottom of our band of values. The scatter in the data is not more than we would have intuitively estimated on the basis of coal heterogeneity. This is because these results are obtained by ratioing infrared bands and thus cancelling errors from a number of sources (eg. weighing, insufficient grinding, improper corrections for moisture and mineral contents of the coal). When we consider values of H_{ar} and H_{al} separately, however, these errors return with a bang, as can be seen in the plots shown in figure 3 for the vitrinite concentrates. This, unfortunately, has dire consequences for the calculation of structural parameters.

Before turning our attention to the calculation of these parameters, we will briefly mention measurements of methyl groups by FT-ir. The most easily recognized group frequencies for methyl groups are the stretching modes near 2960 and 2870 cm^{-1} and the symmetric bending mode near 1380 cm^{-1} . The overlap of these bands with other modes is severe and even sophisticated curve resolving procedures cannot entirely separate out the contributions of other functional groups. When methyl groups are attached to aromatic rings, however, a weak overtone band appears near 2730 cm^{-1} (17). This band is well separated from other modes and the precision of FT-ir measurements is such that its band area should be measurable with reasonable accuracy. The process is not entirely straightforward due to problems with establishing a baseline in this region of a typical coal spectrum (the position of the baseline can dramatically affect the measured area of an infrared band). This problem and its solution is discussed elsewhere (18). An absorption coefficient for this band was determined from model compounds. Unsurprisingly, this coefficient did not vary significantly amongst a variety of methyl substituted aromatic materials. This is because many of the methyl vibrational modes are not sensitive to the size and nature of the aromatic entity to which it is attached. We determined that for vitrinite concentrates obtained from bituminous coals the %C found as methyl groups attached to aromatic units varied between 3 and 5% (with one or two outside this range). These numbers agree very well with the total methyl content recently determined by ^{13}C nmr for some of the same vitrinites by Pugmire and Grant (15). Presumably, in vitrinites there are very few methyl groups present in ethyl, propyl or similar units. (This is not the case for exinites, which are much more aliphatic. We again determine that approximately 4%C is tied up in methyl groups attached to aromatic rings, but nmr analysis indicates a total methyl content of approximately 7%).

Given that we can determine reasonably accurate values for the relative proportions of aliphatic and aromatic carbon from ^{13}C nmr, aliphatic and aromatic hydrogen from FT-ir and methyl group concentration from either or both techniques, what can we calculate and to what extent does it mean anything? Space does not permit us to consider all the equations utilized by Dryden (11,12) and Brown and Ladner (13), but a relatively simple example indicates the problem. The following two equations can be used to describe the distribution of aliphatic groups;

$$H_{al} = H_{CH} + H_{CH_2} + H_{CH_3} \quad (3)$$

$$C_{al} = C_{CH} + C_{CH_2} + C_{CH_3} \quad (4)$$

The concentration of hydrogen and carbon present in aliphatic groups, H_{al} and C_{al} , can be determined from FT-ir and ^{13}C nmr, respectively. The % hydrogen and carbon present in methyl groups, H_{CH_3} and C_{CH_3} , can also be determined as discussed above. This leaves two equations in two unknowns. Consequently, we should be able to determine the distribution of aliphatic species in any particular coal. Consider, however, a typical example. A vitrinite concentrate (PSMC 71, 85.2%C) with $f = 0.73$, $H_{al} = 3.5\%$ and $C_{CH_3} = 3.6\%$. Solving equations (3) and (4) gives values of $C_{CH_2} = 11.8\%$ and $C_{CH} = 7.6\%$. Now consider the effects of relatively modest errors. For example, if we optimistically decide that f is equal to 0.73 ± 0.2 and H_{al} is equal to $3.5 \pm 0.2\%$, we can determine a range of values of C_{CH_2} and C_{CH} corresponding to the upper and lower limits of these values. The values of C_{CH} now fall in the range 15.1% to 2.2% while C_{CH_2} falls in the range 4.5% to 16.2%! Clearly for any single sample even small errors multiply to such an extent that it is not possible to define structural parameters with any degree of precision or confidence.

This situation is not confined to the simple example given above. For example, he previously (9) used the Brown-Ladner equation (13) to calculate the aliphatic hydrogen to carbon atomic ratio, H_{al}/C_{al} :

$$f_a = [C/H - H^*_{al}/(H_{al}/C_{al})]/C/H \quad (5)$$

where H^*_{al} is the fraction of total hydrogen present as aliphatic groups. Assuming errors of approximately $\pm 5\%$ in values of f , it was found that proportionally much larger errors were calculated in H_{al}/C_{al} , these errors increasing proportionally with rank. This is because H_{al}/C_{al} actually varies with the reciprocal of $(1-f)$, so that errors in f become increasingly significant. [For example, even small errors in f for a high rank coal, say $0.9 - 0.02$ or -2% results in much larger errors in $(1-f)^{-1}$, $0.1 - 0.02$ or -20%].

Clearly, the accurate calculation of structural parameters for any specific coal is almost pointless, given the precision of the data presently available. Nevertheless, broad averages and trends as a function of rank can be determined. If we take the plots of f , H_{al} , H , etc. reproduced in figures 1 thru 3, then we can draw lines through the data. At any particular value of %C we can then read off these plots values that represent an "average" parameter value for coals of that rank. These average values can then be used to calculate structural parameters. This procedure is limited and unsatisfactory, but given the major effects experimental errors have on the data, it is the best we can do at this time. If nothing else they show trends as a function of rank. As an example a plot of the distribution of aliphatic CH groups is shown in figure 4. It can be seen that the proportion of CH_2 to CH groups increases as a function of rank, while the experimentally determined %C as CH_3 groups remains approximately constant.

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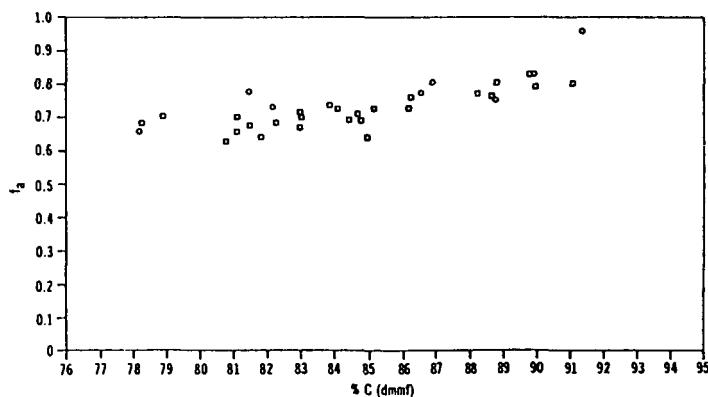


Figure 1. Plot of fraction aromaticity, f_a , vs %C dmmf for a set of vitrinite concentrates.

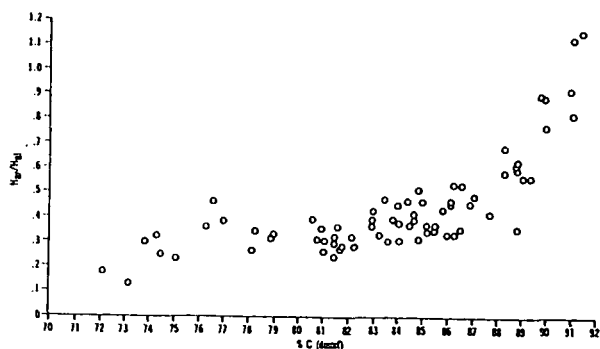


Figure 2. Plot of the ratio of aromatic to aliphatic hydrogen, H_{ar}/H_{al} , determined for a set of coals and vitrinite concentrates.

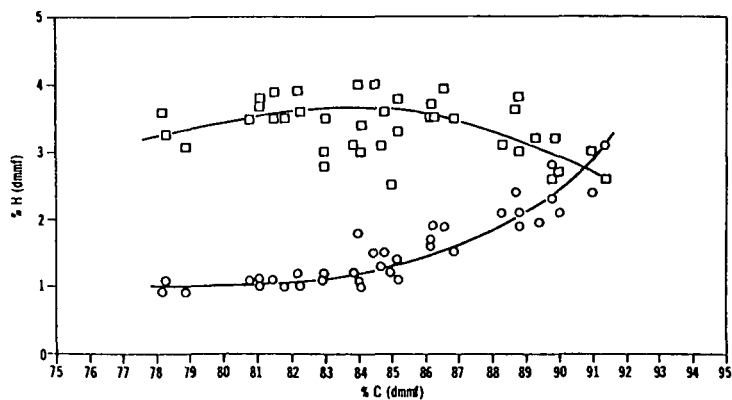


Figure 3. Plot of %H in aliphatic groups (top) and %H in aromatic groups (bottom) vs %C dmnf for a set of vitrinite concentrates.

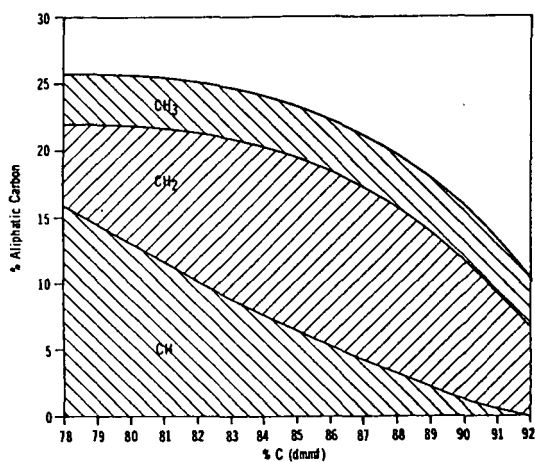


Figure 4. Plot of distribution of aliphatic groups as a function of rank of a set of vitrinite concentrates.